Comment on Phys. Stat. Sol. (b) 236 (2003) 281 paper by A. M. Oles "Orbital ordering and orbital fluctuations in transition metal oxides"

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We argue that the $^3A_2$ state considered by Oles in Phys. Stat. Sol. (b) 236 (2003) 281 for the d^2 system occurring in the V^{3+} ion in V_2O_3 and $LaVO_3$ as well as in Ti^{2+} ion in TiO and in many other oxides is wrong. The proper ground state is $^3T_{1g}$ - its 9-fold degeneracy is further split in a crystal by intra-atomic spin-orbit interactions and lattice distortions.

Keywords: crystal field, ground V^{3+} ion, d^2 system, spin-orbit coupling, V_2O_3

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Oles in Phys. Stat. Sol. (b) 236 (2003) 281 [1] presents in Fig. 1 excitations spectra for d^8, d^5, d^2 and d^3 systems. According to Fig. 1b excitations spectra in cubic transition metal oxides for d^2 ions have the ground state $^3A_2$ and higher states $^1T_2$, ^1E and $^1A_1$. According to us this ground state is wrong. For the d^2 system in the octahedral anion surrounding the ground state is $^3T_{1g}$ [2, 3]. The state $^3T_{1g}$ is completely different from the Oles ground state $^3A_2$ - the latter has 3-fold degeneracy whereas the former - 9-fold degeneracy. The state $^3A_2$ is the orbital singlet whereas $^3T_{1g}$ is an orbital triplet. This difference is of fundamental importance in modern solid-state physics owing to widely discussed properties of V_2O_3, $LaVO_3$ and YVO_3 not mention TiO or CrO_2. Behind these states is completely different physics. By this Comment we would like to clarify the ground state of the V^{3+} and Ti^{2+} ions in the octahedral crystal field. Despite of more than 50 years of intensive studies of, say, V_2O_3, its ground state has not been established yet becoming at present a subject of the very strong controversy.

The many-electron $^3T_{1g}$ state as the ground state of the d^2 system occurring in V_2O_3 has been calculated by us for the SCES-02 Conference [4]. We have considered the V^{3+} ion in the octahedral anion surroundings and, unlike others, with taking into account strong intra-atomic electron correlations of the intra-atomic nature and the spin-orbit coupling [2, 3, 4]. The 9-fold

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degeneracy of the $^3T_{1g}$ subterm is further split in a crystal by intra-atomic spin-orbit interactions and lattice distortions [2, 3]. It is plausible that the $^3T_{1g}$ ground octahedral subterm in a solid compound, where $3d$ atoms are the full part of the crystallographic lattice, is in agreement with the ground state of the $3d^2$ system embedded in the lattice as impurities [5]. Most scientists work in the completely different description for $3d$ electrons ignoring the atomic integrity of the $3d$ ion, what is visible in no usage of the atomic many-electron notation. In a recent paper by Horsch et al. [6], of which Oles is the coauthor, a state $^3T_2$ is once mentioned to be the ground state of V^{3+} ions in V_2O_3. However, there was no explanation for the change of the ground state compared to the commented paper. The commented paper was even not mentioned.

Note added after the referee reports. Both referees admit that "the ground state of the d^2(t_{2g})-system (Ti^{2+} and V^{3+} ion) is 9-fold degenerate $^3T_1$ level" but one of them claims that it "is only improper labeling" that according to the referee "has absolutely no consequence on the results obtained by Oles". We cannot agree that it is only an improper labeling. The commented paper was prepared (submission date: July 1, 2002) at the same time when our submission (May 31, 2002) to the SCES-02 Conference [4] has been rejected (December 23, 2002) by the Publishing Committee as presenting incorrectly the many-electron $^3T_{1g}$ state as the ground state of V^{3+} ions in V_2O_3. Oles was a member of the Organizing Committee of the SCES-02 as well as the leading member of the Editorial Board. Thus, it is not "only improper labeling" as the referee would like. Oles has worked with the $^3A_2$ ground state making use of the d^8 ground state and the hole-particle symmetry as is written on p. 282, line 14 top of the commented paper and in his recalled paper [7] in the commented paper as Ref. 8. In fact, the wrong Fig. 1 is directly taken from that paper.

We also cannot agree with the second point of the referee. A theory that does not distinguish between the 3-fold degenerate $^3A_2$ ground state and the 9-fold degenerate $^3T_{1g}$ ground state surely is not physically useful.

At the end we would like to add that we somehow like the Oles ground state as it is already a many-electron state what we consider as a large progress towards our understanding within the quantum atomistic solid-state approach (QUASST) [8, 9]. Both our and Oles approach contrasts a customary qualitative consideration with single-electron t_{2g}/e_g states and/or with $3d$ bands of the 1-5 eV width.

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